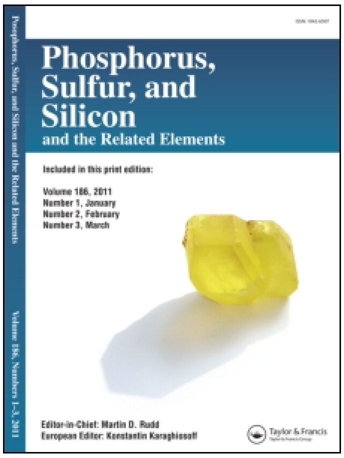


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

One-Pot Synthesis of Stable Phosphorus Ylides by Three-Component Reaction between Dimethyl Acetylenedicarboxylate, Semicarbazones, and Triphenylphosphine

Mohammad Anary-Abbasinejad[a]; Hossein Anaraki-Ardakani[a]; Hossein Hosseini-Mehdiabad[a]
[a] Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran

To cite this Article Anary-Abbasinejad, Mohammad , Anaraki-Ardakani, Hossein and Hosseini-Mehdiabad, Hossein(2008) 'One-Pot Synthesis of Stable Phosphorus Ylides by Three-Component Reaction between Dimethyl Acetylenedicarboxylate, Semicarbazones, and Triphenylphosphine', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 6, 1440 — 1446

To link to this Article: DOI: 10.1080/10426500701670725

URL: http://dx.doi.org/10.1080/10426500701670725

Phosphorus, Sulfur, and Silicon, 183:1440–1446, 2008

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701670725

One-Pot Synthesis of Stable Phosphorus Ylides by Three-Component Reaction between Dimethyl Acetylenedicarboxylate, Semicarbazones, and Triphenylphosphine

Mohammad Anary-Abbasinejad,
Hossein Anaraki-Ardakani,
and Hossein Hosseini-Mehdiabad
Department of Chemistry, Islamic Azad University, Yazd Branch,
Yazd, Iran

Protonation of the reactive 1:1 intermediate, produced in the reaction between dimethyl acetylenedicarboxylate and triphenylphosphine, by aromatic aldehyde semicarbazones leads to vinylphosphonium salts, which undergo Michael addition with the conjugate base of the NH-acid to produce highly functionalized, salt free phosphorus ylides in excellent yields.

Keywords Acetylenic esters; semicarbazones; phosphorus ylides; triphenylphosphine; NH-acids

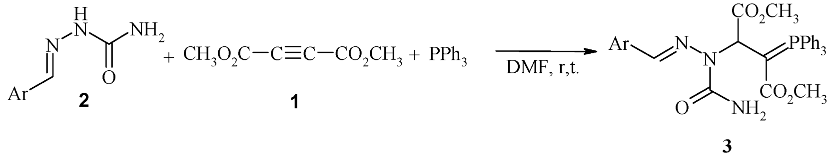
INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis.[1–7] Several methods have been developed for the preparation of phosphorus ylides. The ylides are usually prepared by treatment of an appropriate phosphonium salt with a base; the corresponding phosphonium salts are usually obtained from the phosphine and an alkyl halide.[1,2] Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins.[1] The phosphonium salts are most often converted to the ylides by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. Recently, the reaction of acetylenic esters with triphenylphosphine in the presence of organic N-H acids has been reported to produce nitrogen containing phosphorus ylides.[8] Here we report

Received 9 August 2007; accepted 8 September 2007.

Address correspondence to Mohammad Anary-Abbasinejad, Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran. E-mail: mohammadanary@yahoo.com

an efficient synthetic route to stable phosphorus ylides using triphenylphosphine, aldehyde semicarbazones and dimethyl acetylenedicarboxylate. The reaction of semicarbazone **2** with acetylenic ester **1** in the presence of triphenylphosphine leads to the corresponding ylide **3** in good yields (Scheme 1).

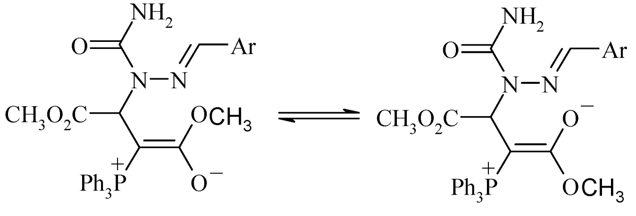


3	Ar	Yield [%]
a	C_6H_5	95
b	$3\text{-}CH_3OC_6H_4$	91
c	$4\text{-}CH_3OC_6H_4$	94
d	$2\text{-}ClC_6H_4$	90
e	$2\text{-}BrC_6H_4$	95
f	$4\text{-}ClC_6H_4$	98

SCHEME 1

RESULTS AND DISCUSSION

The structures of compounds **3a–f** result from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of the ylides **3** are fairly similar and display molecular ion peaks. The NMR spectra of ylides **3a–f** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the C,C-bond due to partial double-bond character is slow on the NMR time scale at room temperature (Scheme 2).



SCHEME 2

The ^{1}H NMR spectrum of **3a** shows two sharp lines ($\delta = 2.93$, 3.74 ppm) for the methyl groups of the major isomer, along with a signal for the methine proton at 5.52 ppm, which appears as a doublet ($^3J_{PH} = 16$ Hz). The HC=N proton appears at $\delta = 8.21$ ppm and the aromatic protons show multiplets at $\delta = 7.30$–7.80 ppm. The corresponding signals for the minor isomer appear at $\delta = 3.65$, 3.77 ppm for the methyl groups and at $\delta = 5.42$ ppm ($^3J_{PH} = 16$ Hz) for the methine proton. The ^{31}P NMR spectrum of compound **3a** displays two signals at 23.3 and 22.9 ppm for the major and the minor isomer, respectively. These shifts are similar to those observed for other stable phosphorus ylides.[9,10] The structural assignments made on the basis of the NMR spectra of compound **3a** are supported by its IR spectrum. The ester carbonyl groups exhibit absorption bands at 1743 and 1683 cm^{-1}. The N-H stretching absorption bands appear at 3390–3255 cm^{-1}.

Based on the well-established chemistry of trivalent phosphorus nucleophiles,[1–7] it is reasonable to assume that ylides **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid. Then, the positively charged ion is attacked by the anion of the NH-acid to form the phosphoranes **3**.

In summary, phosphorus ylides may be prepared by a simple, one-pot three-component reaction of dimethyl acetylenedicarboxylate, aldehyde semicarbazones, and triphenylphosphine. The present method carries the advantage that not only the reaction is performed under neutral conditions but also that the substances can be mixed without any activation or modification.

EXPERIMENTAL

All melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a BRUKER DRX-300 AVANCE spectrometer at 300.1, 75.46, and 121.49 MHz, respectively. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in d_6-DMSO solution using TMS as internal standard (^{1}H, ^{13}C) or 85% H_3PO_4 as external standard (^{31}P). The chemicals used in this study were purchased from Fluka and were used without further purification.

General Procedure

To a magnetically stirred solution of triphenylphosphine (0.52 g, 2 mmol) and the semicarbazone (2 mmol) in DMF (10 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in DMF (3 mL) at room temperature over a period of 2 min. The reaction mixture was then stirred for 30 min. Water (50 mL) was added and the precipitate was filtrated and recrystallized from ethyl acetate / hexane mixture.

Dimethyl 2-Triphenylphosphanylidene 3-(5-Phenyl-1,3,4-triaza-4-buten-2-one-3-yl)- butandioic Acid (3a)

Yield: 1.0 g (90%); colorless crystals; m.p. 180–181°C. IR (KBr) (ν_{max}, cm^{-1}): 3390, 3335, 3255 (NH_2) 1743, 1683, 1633 (C=O). Calcd. for $C_{32}H_{30}N_3O_5P$: C, 67.72; H, 5.33; N, 7.40%. Found: C, 67.5; H, 5.5; N, 7.3%. MS (m/z,%): 567 (M, 3). Major isomer (80%): ^{1}H NMR (d$_6$-DMSO): δ = 2.93 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.52 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.33 (broad s, 2H, NH_2), 7.30–7.80 (m, 20H, arom-H), 8.21 (s, 1H, HC=N). ^{13}C NMR (d$_6$-DMSO): δ = 37.4 (d, $^1J_{PC}$ = 122 Hz, C=P), 49.3 (OCH_3), 52.5 (OCH_3), 57.6 (d, $^2J_{PC}$ = 16 Hz, CH), 125.5 (d, $^1J_{PC}$ = 91 Hz), 128.3 (d, $^2J_{PC}$ = 12 Hz), 132.8 (d, $^4J_{PC}$ = 2 Hz), 133.6 (d, $^3J_{PC}$ = 10 Hz), 127.1 (C_6H_5), 129.7 (C_6H_5), 136.3 (C_6H_5), 139.3 (C_6H_5), 146.1 (HC=N), 156.6 (C=O), 168.9 (d, $^2J_{PC}$ = 12 Hz), 172.4 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d$_6$-DMSO): δ = 23.3.Minor isomer (20%): ^{1}H NMR (d$_6$-DMSO): δ = 3.65 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.42 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.33 (broad s, 2H, NH_2), 7.30–7.80 (m, 20H, arom-H), 8.15 (s, 1H, HC=N). ^{13}C NMR (d$_6$-DMSO): δ = 37.5 (d, $^1J_{PC}$ = 122 Hz, C=P), 50.5 (OCH_3), 52.8 (OCH_3), 57.6 (d, $^2J_{PC}$ = 16 Hz, CH), 125.1 (d, $^1J_{PC}$ = 91 Hz), 129.7 ($^2J_{PC}$ = 12 Hz), 132.6 (d, $^4J_{PC}$ = 2 Hz), 133.9 (d, $^3J_{PC}$ = 10 Hz), 127.2 (C_6H_5), 129.0 (C_6H_5), 135.9 (C_6H_5), 139.7 (C_6H_5),145.3 (HC=N), 157.3 (C=O), 169.1 (d, $^2J_{PC}$ = 12 Hz), 172.7 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d$_6$-DMSO): δ = 22.9.

Dimethyl 2-Triphenylphosphanylidene 3-(5-(3-Methoxyphenyl)-1,3,4-triaza-4-buten-2-one-3-yl)butandioic Acid (3b)

Yield: 1.1 g (91%); colorless crystals; m.p. 180–182°C. IR (KBr) (ν_{max}, cm^{-1}): 3490, 3335, 3300, (NH), 1751, 1779, 1637 (C=O). Calcd. for $C_{33}H_{32}N_3O_6P$: C, 66.32; H, 5.40; N, 7.03%. Found: C, 66.2; H, 5.5; N, 7.1%. MS (m/z,%): 597 (M, 5). Major isomer (85%): ^{1}H NMR (d$_6$-DMSO): δ = 2.94 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 5.52 (d, $^3J_{PH}$ = 16 Hz, 1H), 5.76 (broad s, 2H, NH_2), 7.0–7.6 (m, 19H, arom-H), 8.17 (s, 1H, HC=N). ^{13}C NMR (d$_6$-DMSO): δ = 37.5 (d, $^1J_{PC}$ = 123 Hz, C=P), 49.2 (OCH_3), 52.5 (OCH_3), 55.7 (OCH_3), 57.5 (d, $^2J_{PC}$ = 16 Hz, CH), 125.6 (d, $^1J_{PC}$ = 91 Hz), 129.3 ($^2J_{PC}$ = 12 Hz), 132.8 (d, $^4J_{PC}$ = 2 Hz), 133.6 (d, $^3J_{PC}$ = 10 Hz), 111.3 (C_6H_4), 115.8 (C_6H_4), 120.1 (C_6H_4), 130.2 (C_6H_4), 137.8 (C_6H_4), 146.1 (C_6H_4), 156.5 (HC=N), 160.1 (C=O), 169.1

(d, $^2J_{PC}$ = 12 Hz), 172.5 (d, $^3J_{CP}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.3.Minor isomer (15%): ^{1}H NMR (d_6-DMSO): δ = 3.55 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.46 (d, $^3J_{PH}$ = 16 Hz, 1H), 5.76 (broad s, 2H, NH_2), 7.0–7.6 (m, 19H, arom-H), 8.12 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 37.6 (d, $^1J_{PC}$ = 123 Hz,C=P), 50.4 (OCH_3), 52.7 (OCH_3), 55.3 (OCH_3), 57.5 (d, $^2J_{PC}$ = 16 Hz, CH), 125.1 (d, $^1J_{PC}$ = 91 Hz), 129.2 ($^2J_{PC}$ = 12 Hz), 132.6 (d, $^4J_{PC}$ = 2 Hz), 133.6 (d, $^3J_{PC}$ = 10 Hz), 111.1 (C_6H_4), 115.9 (C_6H_4), 120.4 (C_6H_4), 130.1 (C_6H_4), 139.6 (C_6H_4), 145.7 (C_6H_4), 156.6 (HC=N), 160.0 (C=O), 169.1 (d, $^2J_{PC}$ = 12 Hz), 172.5 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.0.

Dimethyl 2-Triphenylphosphanylidene 3-(5-(4-Methoxyphenyl) -1,3,4-triaza-4-buten-2-one-3-yl)butandioic Acid (3c)

Yield: 1.1 g (94%); colorless crystals; m.p. 185–186°C. IR (KBr) (ν_{max}, cm^{-1}): 3475, 3335, 3270 (NH), 1741, 680, 1620 (C=O). Calcd. for $C_{33}H_{32}N_3O_6P$: C, 66.32; H, 5.40; N, 7.03%. Found: C, 66.3; H, 5.4; N, 7.2%. MS (m/z,%): 597 (M, 3). Major isomer (73%): ^{1}H NMR (d_6-DMSO): δ = 2.94 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.55 (d, $^3J_{PH}$ = 16 Hz,1H), 6.20 (broad s, 2H, NH_2), 7.0–7.7 (m, 19H, arom-H), 8.24 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 37.5 (d, $^1J_{PC}$ = 123 Hz, C=P), 49.2 (OCH_3), 52.4 (OCH_3), 55.7 (OCH_3), 57.7 (d, $^2J_{PC}$ = 16 Hz, CH), 125.7 (d, $^1J_{PC}$ = 91 Hz), 129.1 ($^2J_{PC}$ = 12 Hz), 132.7 (d, $^4J_{PC}$ = 2 Hz), 133.7 (d, $^3J_{PC}$ = 10 Hz), 114.6 (C_6H_4), 128.6 (C_6H_4), 128.8 (C_6H_4), 146.5 (C_6H_4), 156.6 (HC=N), 160.6 (C=O), 169.9 (d, $^2J_{PC}$ = 12Hz), 172.6 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.3.Minor isomer (27%): ^{1}H NMR (d_6-DMSO): δ = 3.56 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.50 (d, $^3J_{HP}$ = 16 Hz, 1H), 6.20 (broad s, 2H, NH_2), 7.0–7.7 (m, 19H, arom-H), 8.18 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 37.5 (d, $^1J_{PC}$ = 123 Hz, C=P), 50.3 (OCH_3), 52.7 (OCH_3), 55.3 (OCH_3), 57.7 (d, $^2J_{PC}$ = 16 Hz, CH), 125.5 (d, $^1J_{PC}$ = 91 Hz), 129.1 ($^2J_{PC}$ = 12 Hz), 132.6 (d, $^4J_{PC}$ = 2 Hz), 133.8 (d, $^3J_{PC}$ = 10 Hz), 114.5 (C_6H_4), 128.6 (C_6H_4), 128.8 (C_6H_4), 146.1 (C_6H_4), 156.7 (HC=N), 160.8 (C=O), 169.9 (d, $^2J_{PC}$ = 12 Hz), 172.6 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.0.

Dimethyl 2-Triphenylphosphanylidene 3-(5-(2-Chlorophenyl)-1,3,4-triaza-4-buten-2-one-3-yl)butandioic Acid (3d)

Yield: 1.1 g (90%); colorless crystals; m.p. 168–169°C. IR (KBr) (ν_{max}, cm^{-1}): 3385, 3341, 3270 (NH_2), 1745, 1679, 1641 (C=O). Calcd. for $C_{32}H_{29}ClN_3O_5P$: C, 63.84; H, 4.86; N, 6.98%. Found: C, 63.8; H, 4.7; N, 6.7%. MS (m/z,%): 602 (M, 3). Major isomer (80%): ^{1}H NMR (d_6-DMSO):

δ = 2.96 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.57 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.35 (broad s, 2H, NH_2), 7.3–8.2 (m, 19H, arom-H), 8.43 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 35.3 (d, $^1J_{PC}$ = 122 Hz, C=P), 49.2 (OCH_3), 52.4 (OCH_3), 57.9 (d, $^2J_{PC}$ = 16 Hz, CH), 126.0 (d, $^1J_{PC}$ = 91 Hz), 129.2 ($^2J_{PC}$ = 12 Hz), 132.8 (d, $^4J_{PC}$ = 2 Hz), 133.7 (d, $^3J_{PC}$ = 10 Hz), 127.5 (C_6H_4), 128.1 (C_6H_4), 130.2 (C_6H_4), 130.5 (C_6H_4), 133.2 (C_6H_4), 134.1 (C_6H_4), 139.8 (HC=N), 156.0 (C=O), 168.5 (d, $^2J_{PC}$ = 12 Hz), 172.2 (d, $^3J_{PC}$ = 16 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.2.Minor isomer (20%):^{1}H NMR (d_6-DMSO): δ = 3.37 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.57 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.35 (broad s, 2H, NH_2), 7.3–8.2 (m, 19H, arom-H), 8.57 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 36.2 (d, $^1J_{PC}$ = 122 Hz, C=P), 50.8 (OCH_3), 52.4 (OCH_3), 57.5 (d, $^2J_{PC}$ = 16 Hz, CH), 125.1 (d, $^1J_{PC}$ = 91 Hz), 129.1 ($^2J_{PC}$ = 12 Hz), 132.5 (d, $^4J_{PC}$ = 2 Hz), 133.6 (d, $^3J_{PC}$ = 10 Hz), 127.5 (C_6H_4), 128.2 (C_6H_4), 130.1 (C_6H_4), 130.8 (C_6H_4), 133.1 (C_6H_4), 133.9 (C_6H_4), 139.2 (HC=N), 157.1 (C=O), 169.3 (d, $^2J_{PC}$ = 12 Hz), 172.3 (d, $^3J_{PC}$ = 16 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.1.

Dimethyl 2-Triphenylphosphanylidene 3-(5-(2-Bromophenyl)-1,3,4-triaza-4-buten-2-one-3-yl)butandioic Acid (3e)

Yield: 1.2 g (95%); colorless crystals; m.p. 189–190°C. IR (KBr) (ν_{max}, cm^{-1}): 3460, 3335, 3270, 3200 (NH_2), 1743, 1712 (C=O). Calcd. for $C_{32}H_{29}BrN_3O_5P$: C, 59.45; H, 4.52; N, 6.50%. Found: C, 59.6; H, 4.5; N, 6.7%. MS (m/z,%): 646 (M, 1). Major isomer (70%): ^{1}H NMR (d_6-DMSO): δ = 2.95 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 5.57 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.32 (broad s, 2H, NH_2), 7.3–8.3 (m, 19H, arom-H), 8.32 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 36.1 (d, $^1J_{PC}$ = 122 Hz, C=P), 49.4 (OCH_3), 52.4 (OCH_3), 58.0 (d, $^2J_{PC}$ = 16 Hz, CH), 126.3 (d, $^1J_{PC}$ = 91 Hz), 129.2 ($^2J_{PC}$ = 12 Hz), 132.8 (d, $^4J_{PC}$ = 1 Hz), 133.7 (d, $^3J_{PC}$ = 10 Hz), 123.2 (C_6H_4), 128.1 (C_6H_4), 128.5 (C_6H_4), 130.8 (C_6H_4), 133.8 (C_6H_4), 135.6 (C_6H_4), (C_6H_4), 141.5 (HC=N), 156.6 (C=O), 168.3 (d, $^2J_{PC}$ = 12 Hz), 172.0 (d,$^3J_{PC}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.3.Minor isomer (20%): ^{1}H NMR (d_6-DMSO): δ = 3.47 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 5.57 (d, $^3J_{PH}$ = 16 Hz, 1H), 6.32 (broad s, 2H, NH_2), 7.3–8.3 (m, 19H, arom-H), 8.47 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): δ = 37.5 (d, $^1J_{PC}$ = 122 Hz, C=P), 51.1 (OCH_3), 52.8 (OCH_3), 58.0 (d, $^2J_{PC}$ = 16 Hz, CH), 125.6 (d, $^1J_{PC}$ = 91 Hz), 129.0 (d, $^2J_{PC}$ = 12 Hz), 132.5 (d, $^4J_{PC}$ = 1 Hz), 133.7 (d, $^3J_{PC}$ = 10 Hz), 123.2 (C_6H_4), 128.2 (C_6H_4), 128.7 (C_6H_4), 131.1 (C_6H_4), 133.8 (C_6H_4), 135.3 (C_6H_4), 141.4 (HC=N), 157.1 (C=O), 169.4 (d, $^2J_{PC}$ = 12 Hz), 172.3 (d, $^3J_{PC}$ = 17 Hz). ^{31}P NMR (d_6-DMSO): δ = 23.1.

Dimethyl 2-Triphenylphosphanylidene 3-(5-(4-Chlorophenyl)-1,3,4-triaza-4-buten-2-one-3-yl)butandioic Acid (3f)

Yield: 1.2 g (98%); colorless crystals; m.p. 171–172°C. IR (KBr) ($\nu_{\max}$, cm^{-1}): 3490, 3363, 3256 (NH_2), 1743, 1680, 1651 (C=O). Calcd. for $C_{32}H_{29}ClN_3O_5P$: C, 63.84; H, 4.86; N, 6.98%. Found: C, 63.7; H, 4.8; N, 7.0%. MS (m/z,%): 602 (M, 1). Major isomer (80%): ^{1}H NMR (d_6-DMSO): $\delta = 2.94$ (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.57 (d, $^{3}J_{PH} = 16$ Hz, 1H), 6.32 (broad s, 2H, NH_2), 7.3–7.8 (m, 19H, arom-H), 8.20 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): $\delta = 37.1$ (d, $^{1}J_{PC} = 122$ Hz, C=P), 49.3 (OCH_3), 52.5 (OCH_3), 57.3 (d, $^{2}J_{PC} = 16$ Hz, CH), 126.2 (d, $^{1}J_{PC} = 91$ Hz), 129.2 (d, $^{2}J_{PC} = 12$ Hz), 132.8 (d, $^{4}J_{PC} = 2$ Hz), 133.7 (d, $^{3}J_{PC} = 10$ Hz), 128.6 (C_6H_4), 129.1 (C_6H_4), 134.2 (C_6H_4), 135.3 (C_6H_4), 144.3 (HC=N), 156.3 (C=O), 168.9 (d, $^{2}J_{PC} = 12$ Hz), 172.4 (d, $^{3}J_{PC} = 17$ Hz). ^{31}P NMR (d_6-DMSO): $\delta = 23.3$.Minor isomer (20%): ^{1}H NMR (d_6-DMSO): $\delta = 3.56$ (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.52 (d, 1H, $^{3}J_{PH} = 16$ Hz), 6.32 (broad s, 2H, NH_2), 7.3–7.8 (m, 19H, arom-H), 8.12 (s, 1H, HC=N). ^{13}C NMR (d_6-DMSO): $\delta = 37.1$ (d, $^{1}J_{PC} = 122$ Hz, C=P), 50.4 (OCH_3), 52.5 (OCH_3), 57.3 (d, $^{2}J_{PC} = 16$ Hz, CH), 125.5 (d, $^{1}J_{PC} = 91$ Hz), 129.2 (d, $^{2}J_{PC} = 12$ Hz), 132.8 (d, $^{4}J_{PC} = 2$ Hz), 133.7 (d, $^{3}J_{PC} = 10$ Hz), 128.5 (C_6H_4), 128.7 (C_6H_4), 134.4 (C_6H_4), 134.9 (C_6H_4), 143.3 (HC=N), 156.3 (C=O), 168.9 (d, $^{2}J_{PC} = 12$ Hz), 172.4 (d, $^{3}J_{PC} = 17$ Hz). ^{31}P NMR (d_6-DMSO): $\delta = 23.0$.

REFERENCES

[1] D. E. C. Corbridge, *Phosphorus an Outline of the Chemistry, Biochemistry, and Uses* (Elsevier, Amsterdam, 1995), 5th ed.

[2] R. Engel, *Synthesis of Carbon-Phosphorus bonds* (CRC Press, Boca Raton, 1988).

[3] O. I. Kolodiazhnyi, *Russ. Chem. Rev.*, **66,** 225 (1997).

[4] H. J. Bestmann and R. Zimmermann, *Top. Curr. Chem.*, **109,** 85 (1983).

[5] B. E. Maryano and A. B. Reits, *Chem. Rev.*, **89,** 863 (1989).

[6] K. M. Pietrusiewiz and M. Zablocka, *Chem. Rev.*, **94,** 1375 (1994).

[7] R. A .Aitken, H. Herion, A. Janosi, N. Karodia, S. Raut, V. S. Seth, I. J. Shannon, and F. C. Smith, *J. Chem. Soc. Perkin Trans.*, **1,** 2467 (1994).

[8] (a) I. Yavari, M. T. Maghsoodlou, H. Djahaniani, and N. Hazeri, *J. Chem. Res.* (S), 216 (1999); (b) M. Adib, M. Mostofi, K. Ghanbary, and H. Bijanzadeh, *Synthesis*, **10,** 1663 (2005).

[9] J. C. Tebby, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, J. C. Verkade and L. D. Quin, Eds., (VCH, Weinheim, 1987), Ch. 1, pp 1–60.

[10] E. Vedejs and K. A. J. Snoble, *J. Am. Chem. Soc.*, **95,** 5778 (1973).